Ormancılık Araştırma Dergisi
Journal of Forestry Research
2016/2, A, 1:4, 134-143

DOI: http://dx.doi.org/10.17568/oad.19661
Orman Ürünleri/Forest Products
Araştırma makalesi/Research article

Effects of sodium borohydride addition to kraft pulping process of some pine species

Akın SARAÇBAŞI[1*], Prof. Dr. Halil Turgut ŞAHİN[2], Prof. Dr. Arif KARADEMİR[3]

[1]Orman Ağaçları ve Tohumları Islah Araştırma Enstitüsü Müdürlüğü, ANKARA
[2]Süleyman Demirel Üniversitesi, Orman Fakültesi, İSPARTA
[3]Bursa Teknik Üniversitesi, Orman Fakültesi, BURSA

[*]Sorumlu yazar/Corresponding author: akinsaracbasi@ogm.gov.tr, Geliş tarihi/Received: 20.05.2016, Kabul tarihi/Accepted: 26.12.2016

Abstract

The Calabrian pine (*Pinus brutia* Ten.) and Monterey pine (*Pinus radiata* D. Don.) species were pulped using an alternative Sodium borohydride ($NaBH_4$)-Kraft pulping process with the aim of improving delignification and total yield. The effects of reaction conditions on the pulp yield and degree of delignification were evaluated.

The results indicate that adding sodium borohydride to conventional kraft process was effective for improving both delignification and yield of both pine species. It was found that the delignification proceeded more rapidly and more selectively with $NaBH_4$-kraft than it did with conventional kraft alone, giving higher yields at a given kappa number. However, the best Sodium borohydride $NaBH_4$- Kraft pulping condition for the Calabrian pine was found with 16% Active Alkali, 28% Sulfidity and 0.5% $NaBH_4$ level whereas the best pulping conditions for Monterey pine was found with 20% Active Alkali, 26% Sulfidity and 0.7% $NaBH_4$ level.

Key Words: Calabrian pine, Monterey pine, sodium borohydride, Kraft pulping, yield, kappa number, viscocity

Bazı çam türlerinden kraft kağıt hamuru elde etme sürecinde sodyum borhidrür ilavesinin etkileri

Öz

Bu araştırmada, kızılçam (*Pinus brutia* Ten.) ve Monteri çamı (*Pinus radiata* D. Don.) türlerinden toplam verim ve delignifikasyonu geliştirmek amacı ile alternatif bir Sodyum borhidrür (NaBH4)-Kraft kâğıt hamuru elde etme yöntemi üzerinde çalışılmıştır. Delignifikasyon derecesi ve hamur verimi üzerinde reaksiyon koşullarının etkileri değerlendirilmiştir.

Sonuçlar, sodyum borhidrür ilavesinin bilinen Kraft yöntemine göre her iki çam türünün hem verim hem de delignifikasyonunu geliştirmek için daha etkili olduğunu göstermektedir. Sodyum borhidrür ($NaBH_4$)-Kraft yönteminin, geleneksel Kraft yönteminin tek başına verdiği kappa numarası ve yüksek verim açısından, daha hızlı ve daha seçici olduğu düşünülmektedir. Ancak, kızılçam için en iyi Sodyum borhidrür ($NaBH_4$)-Kraft kâğıt hamuru üretim koşulu Aktif Alkali: %16, Sülfidite: %28, $NaBH_4$ oranı: %0,5 iken, Monteri çamı için en iyi Sodyum borhidrür ($NaBH_4$)-Kraft kâğıt hamuru üretim koşulunun ise Aktif Alkali: %20, Sülfidite: %26, $NaBH_4$ Oranı: %0,7 olduğu bulunmuştur.

Anahtar Kelimeler: Kızılçam, Monteri çamı, sodyum borhidrür, Kraft kağıt hamuru, verim, kappa numarası, viskozite

To cite this article (Atıf): SARAÇBAŞI A., ŞAHİN H.T., KARADEMİR A., 2016. Effects of sodium borohydride addition to kraft pulping process of some pine species, Orman Genel Müdürlüğü Ormancılık Araştırma Dergisi, 4(1):134-143 DOI: http://dx.doi.org/10.17568/oad.19661

1. Introduction

Alkaline Kraft pulping process is one of the main chemical pulping methods to delignify almost all lignocellulosic substrates in worldwide. Although Kraft process has very advantages over other pulping systems, it has been already reported by a number of researchers that the Kraft chemical process has some serious environmental and capital problems. Some of the important drawbacks for Kraft pulping are summarized below (Biermann 1993; Smook, 1994; Young, 1997);

-It uses environmentally hazard chemicals (e.g. sulphur compounds) in cooking formulations

-It requires very high energy and water usage,

-It causes air and water pollution.

However, in recent years, an extensive research on new environmentally friendly pulping processes has been carried out to overcome the drawback of Kraft process. These includes the use of organic solvents (organosol pulping), and white rot fungus (biopulping). But none of the unconventional processes have replaced with the conventional methods, only a few of them have a very promising future (Biermann, 1993; Young, 1997).

Turkey has a large portion of the world's boron reserves (72%). However, the use of boron compounds has been increased in Europe and Worldwide. This is due to the fact that the boron based chemicals are usually considered as environmentally friendly, hence can help to reduce environmental pressures and eliminate some problems.

Extensive studies have already been carried out for utilization of boron compounds in wood products and paper industries. For example, Özdemir and Tutuş (2013) proposed that addition of boron compounds during high density fiberboard manufacturing improved the fire retardant and combustion behavior of the panels. Pettersson and Rydholm (1961) proposed that during Kraft pulping of birch wood, addition of 2.0% $NaBH_4$ (aq) causes 5.0-7.0% yield increase. The similar results were reported by Khaustov and his group (1971) for Kraft pulping of larix wood that $NaBH_4$ addition causes approximately 4.0% yield increase. İstek and Gönteki (2009) conducted a similar research for maritime pine that boron addition to Kraft pulping process improved delignification and yield of chemical pulps some level. Çöpür and Tozluoğlu (2007) found that adding small amount boron compound to pulping formulations of Calabrian pine gave some advantageous results. Consistently, almost all researchers reported the total yield and brightness increased while residual lignin content and physical properties of pulps decreased to some level.

Virkola et al. (1981) suggested that the addition of disodium borate (Na_2HBO_3) during alkali pulping affects some advantageous results. Bujanovic and his group (2003 and 2004) found that the addition of sodium metaborate ($NaBO_2$) during alkali pulping of wood substrate resulting increase yield some level. Tutuş and Usta (2004) reported some advantageous results with adding $NaBH_4$ during CTMP bleaching. They proposed that $NaBH_4$ addition is good enough to get very advantageous results. Gülsoy and Eroğlu (2011) found that addition of $NaBH_4$ during Kraft pulping clearly effects increase of yield and brightness but lowering mechanical properties of papers some level. Tutuş and his friends (2012) studied that addition of boron compounds to Kraft pulping of burned pine wood chips improve some pulp properties.

Hafızoğlu and Deniz (2007) proposed the behavior of $NaBH_4$ compound in pulping condition. They reported that $NaBH_4$ is a reducing agent that blocks reducing end-groups of carbohydrates (i.e. hemicellulose and cellulose) so it converts the aldehyde and keto group to the hydroxyl group by reducing easily. Hence, the carboxyl borohydride in the lactone form is reduced to some extent.

In more recent study, Tutuş and his group (2016) studied addition of boron compounds to Kraft pulping of an orchard wood (*Prunus armeniaca* L). They found that even small amount of addition of boron compounds on cooking formulations has effects on yield improvement and residual lignin content some level.

In this study, alternative approach for pulping of Calabrian and Monterey pine woods involving adding sodium borohydride ($NaBH_4$) in conventional Kraft pulping formulations have been evaluated. Thus, the best pulping parameter were investigated to find highest total yield and brightness while lower residual lignin content (kappa number) at acceptable physical properties of pulp. Hence, the benefits of $NaBH_4$ addition to Kraft system have been discussed.

2. Materials and Methods

The bark-free Calabrian pine *(Pinus brutia* Ten.*)* and Monterey pine (*Pinus radiata* D. Don.*)* woods were cut according to standard chip sizes of 15–20 mm x 1.5–2.0 mm x 20–25 mm dimensions. The moisture content of the wood chips was about 10%, and this moisture ratio was included in the calculation of the raw material to liquor ratio and the chemical concentration. All chemicals were purchased from a chemical company with a purity of at least 95% unless otherwise noted.

Pulping trials were carried out automatically in a controlled manner, on a laboratory medium, with a stainless steel rotating (4 rotation/min) reactor of 15 liter capacity heating by electricity. In each experiment, 500 grams of wood chips were used. The variables of $NaBH_4$-kraft pulping conditions were as follows;

-Wood to liquor ratio: 1/4 (w/v)

-Active alkali (AA): 16-20%

-Sulfidity: 26, 28 and 30%,

-Sodium borohydride ($NaBH_4$) content: 0.0; 0.3; 0.5; 0.7%,

-Temperature: 160 ^{0}C,

-Cooking time: 90 min.

In each condition, test was carried out three times. At the end of the cook, the pulps were washed on the 200 mesh screen with water. The pulp was disintegrated and screened (0.15 mm openings) in a Somerville type screen to find reject and total yield calculated based on oven dry pulp/per gram of oven dry material.

Hand sheets were prepared in accordance with Tappi Standards T205. The pulp hand sheets were tested for the following properties according to Tappi Standard T220: Sheet density (reported as bulk), tensile strength (Tappi T494), burst strength (Tappi T403), and tear strength (Tappi T414). The Kappa number was determined according to Tappi Standard T236. The optical properties of pulps were determined according to Tappi T525. Pulps were refined in laboratory PFI mill until the specified level of freeness level (50 ± 5 ^{0}SR) was reached. For eliminating detrimental effects of residual lignin on viscosity measurements of pulps, chlorite delignification was carried out (Nelson and Irvine, 1992). The viscosity measurements were carried out according to SCAN C16:88 methods. In this standard, pulp was solubilized in 0.5 M copper ethyldiamine (CED) then it was measured with the determined raw viscosimetry property. Then Martin's formulas and tables were utilized to calculate viscosity as cm^3/g^{-1}. The following relations were between viscosity and cellulose's DP (degree of polymerization):

$$DP^{0.905} = 0{,}75 \text{ x viscosity}$$

Both in the process of Kraft pulping from Calabrian and Monterey pine and in measuring the kappa number and viscosity of Kraft pulps, the planned tests for each condition was conducted for three times and VARIANCE analysis (simple) was carried out. The SPSS (Statistical Program for the Social Sciences) was used to analyze results and these are given in Tables and Figures. DUNCAN multiple test was used to check the differences between the pulping conditions.

3. Results and Discussions

The chemical properties of wood substrates used in this study are given in Table 1. It can be seen that both Calabrian and Monterey pine has marginally similar holocellulose (64-65%), lignin (27-28%), Pentozan (9-10%) and 1.0% NaOH solubility (9-11%) properties. However, Calabrian pine has considerably higher alcohol-benzene solubility compared to Monterey pine. This is probably due to the fact that Calabrian pine has known with its high resin content than the other pine species.

Table 1. Chemical constituents of Calabrian pine and Monterey pine.

Wood species	Holocellulose (%)	α-cellulose (%)	Lignin (%)	Pentosan (%)	Ash (%)	Alcohol-benzene solubility (%)	Reference
Calabrian pine	64.52	41.21	27.18	9.23	0.40	-	Göksel, 1981
Calabrian pine	65.46	42.55	27.47	10.00	0.47	7.92	Tank et al., 1990
Monterey pine	64.06	42.75	28.47	9.30	0.20	1.67	Tank et al., 1990

Statistical results using Variance analysis carried out in order to determine the kappa number, viscosity and total yield values of Kraft pulp produced by Calabrian pine chips are shown in Table 2, Table 3 and Table 4.

Table 2. Variance analysis table (for Calabrian pine total pulp yield).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	1217,021	11	110,638	172,957	0,000
Within Groups	15,352	24	0,640		
Total	1232,373	35			

Table 3. Variance analysis table (for Calabrian pine kappa number).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	2320,116	11	210,920	316,410	0,000
Within Groups	15,998	24	0,667		
Total	2336,115	35			

Table 4. Variance analysis table (for Calabrian pine pulp viscocity).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	131876,593	11	11988,781	72,029	0,000
Within Groups	3994,653	24	166,444		
Total	135871,246	35			

Table 2, Table 3 and Table 4 shows that there is a significant difference between the total yield, kappa number and viscosity values of different interaction groups ($p=0,000$; $p<0,05$) within a 95% confidence interval. Duncan multiple test was carried out in order to see the differences between groups and the results are shown in Table 8.

Statistical results using Variance analysis carried out in order to determine the values of kappa number and viscosity, and total yield values of Kraft pulp produced by Monterey pine chips are shown in Table 5, Table 6 and Table 7.

Table 5. Variance analysis table (for Monterey pine total pulp yield).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	836,230	11	76,020	143,750	0,000
Within Groups	12,690	24	0,530		
Total	848,920	35			

Table 6. Variance analysis table (for Monterey pine kappa number).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	1728,313	11	157,119	43,974	0,000
Within Groups	85,752	24	3,573		
Total	1814,066	35			

Table 7. Variance analysis table (for Monterey pine pulp viscosity).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Ratio	P-Value
Between Groups	78279,994	11	7116,363	19,559	0,000
Within Groups	8731,977	24	363,832		
Total	87011,971	35			

Table 5, Table 6 and Table 7 shows that there is a significant difference between the total yield values of different interaction groups ($p=0,000$; $p<0,05$) within a 95% confidence interval. Duncan multiple test was carried out in order to see the differences between groups and the results are shown in Table 9.

The effects of $NaBH_4$ addition into Kraft pulping process at various sulfidity level and obtained results that were analyzed with Duncan tests are summarized in Table 8A-8B and Table 9A-9B. As mentioned above, this study aims to investigate the effect of NaBH4 addition to Kraft pulping considering that it has the highest yield and lower residual lignin content with acceptable strength properties. It can be seen that for Calabrian pine; the highest yield 59.46% was found with 16% AA, 28% sulfidity and 0.5% $NaBH_4$ addition. However, for Monterey pine; the highest yield 71.84% was found with 20% AA, 26% sulfidity and 0.7% $NaBH_4$ level. It can be seen that clear variations for yield between Calabrian and Monterey pine are even at similar pulping conditions. But, it is noteworthy that at similar sulfidity and $NaBH_4$ addition, the Monterey pine shows approx. 5-25% higher yield than Calabrian pine. This could be expected considering that different wood substrates can respond somehow different delignification mechanisms.

The increase in total yield of pulp produced with $NaBH_4$ addition to the Kraft pulping process is in parallel with the results of other studies in literature. The reason of the increase in pulp yield can be explained with the fact that $NaBH_4$ stops the probable peeling reaction during the pulping process.

Many scientists used various methods and different conditions in order to increase the Kraft (sulphate) pulp yield. In these studies, it's determined that many factors such as chemical and anatomical structure of the raw material, chip quality, kind and amount of additional additives etc. significantly affect Kraft pulp yield.

Table 8A. Duncan multiple test table (for Calabrian pine total pulp yield, kappa number, pulp viscosity).

Cooking conditions						
Cooking number and Statistical code	Active alkali (%)	Cooking time (min)	Wood to liquor ratio (w/v)	Temperature (°C)	Sulfidity (%)	$NaBH_4$ content (%)
1,2,3 (111)	16	90	1/4	160	26	0
4,5,6 (211)	16	90	1/4	160	28	0
7,8,9 (311)	16	90	1/4	160	30	0
10,11,12 (112)	16	90	1/4	160	26	0.3
13,14,15 (212)	16	90	1/4	160	28	0.3
16,17,18 (312)	16	90	1/4	160	30	0.3
19,20,21 (113)	16	90	1/4	160	26	0.5
22,23,24 (213)	16	90	1/4	160	28	0.5
25,26,27 (313)	16	90	1/4	160	30	0.5
28,29,30 (114)	16	90	1/4	160	26	0.7
31,32,33 (214)	16	90	1/4	160	28	0.7
34,35,36 (314)	16	90	1/4	160	30	0.7

Table 9A. Duncan multiple test table (for Monterey pine total pulp yield, kappa number, pulp viscosity).

Cooking conditions						
Cooking number and Statistical code	Active alkali (%)	Cooking time (min)	Wood to liquor ratio (w/v)	Temperature (°C)	Sulfidity (%)	$NaBH_4$ content (%)
1,2,3 (411)	20	90	1/4	160	26	0
4,5,6 (511)	20	90	1/4	160	28	0
7,8,9 (611)	20	90	1/4	160	30	0
10,11,12 (412)	20	90	1/4	160	26	0.3
13,14,15 (512)	20	90	1/4	160	28	0.3
16,17,18 (612)	20	90	1/4	160	30	0.3
19,20,21 (413)	20	90	1/4	160	26	0.5
22,23,24 (513)	20	90	1/4	160	28	0.5
25,26,27 (613)	20	90	1/4	160	30	0.5
28,29,30 (414)	20	90	1/4	160	26	0.7
31,32,33 (514)	20	90	1/4	160	28	0.7
34,35,36 (614)	20	90	1/4	160	30	0.7

Table 8B. Duncan multiple test table (for Calabrian pine total pulp yield, kappa number, pulp viscosity).

Yield values			Some chemical properties	
Screened pulp yield (%)	Reject (%)	Total pulp yield (%)	Kappa number	Pulp viscocity (cm^3/g)
40.90 (0.86)	1.91 (0.10)	42.81 (0.86) A	62.79 (1.33) H	948.02 (9.43) G
41.03 (0.77)	2.06 (0.05)	43.09 (0.79) A	63.58 (1.14) H	937.27 (17.30) FG
42.39 (0.87)	2.40 (0.26)	44.77 (1.11) B	65.78 (1.08) I	918.11 (7.16) EF
43.27 (0.25)	2.44 (0.17)	45.38 (0.22) B	61.28 (1.19) G	909.72 (22.40) E
47.59 (0.56)	2.44 (0.50)	50.03 (0.24) C	55.97 (0.24) F	858.52 (17.80) D
48.05 (1.28)	2.48 (0.44)	50.53 (1.60) C	54.81 (0.71) F	849.16 (9.81) CD
50.24 (0.49)	2.20 (0.28)	52.44 (0.26) D	51.08 (0.26) E	830.77 (2.95) BC
56.55 (0.91)	2.91 (0.23)	59.46 (0.69) G	42.05 (0.87) A	771.19 (6.42) A
54.69 (0.34)	2.47 (0.28)	57.16 (0.61) F	45.24 (0.58) C	783.95 (11.16) A
53.75 (1.13)	2.31 (0.37)	55.72 (1.16) E	47.49 (0.44) D	818.28 (6.15) B
56.02 (0.25)	2.04 (0.41)	58.13 (0.20) FG	43.51 (0.36) B	774.08 (18.40) A
53.52 (0.14)	2.0 (0.22)	55.52 (0.35) E	48.45 (0.60) D	822.08 (5.47) B

*The numbers in phrantheses are standard deviations
**The same letters on the same columns show that statistically there is not a significant difference within a 95% confidence interval.

Table 9B. Duncan multiple test table (for Monterey pine total pulp yield, kappa number, pulp viscosity).

Yield values			Some chemical properties	
Screened pulp yield (%)	Reject (%)	Total pulp yield (%)	Kappa number	Pulp viscocity (cm^3/g)
53.25 (0.28)	2.43 (0.11)	55.68 (0.36) A	75.68 (2.68) EF	880.89 (12.97) H
54.05 (0.55)	2.48 (0.17)	56.54 (0.60) AB	76.72 (2.34) F	867.91 (14.98) GH
55.18 (0.43)	2.41 (0.12)	57.60 (0.45) C	78.24 (1.59) F	848.90 (7.78) FGH
58.80 (0.45)	2.36 (0.12)	61.16 (0.55) C	74.84 (1.28) EF	838.95 (11.66) EFG
60.65 (0.80)	2.16 (0.13)	62.88 (0.95) D	73.26 (1.07) E	825.82 (7.80) DEF
59.34 (1.10)	2.17 (0.26)	61.51 (0.85) C	69.04 (0.56) D	805.29 (4.62) CDE
62.75 (0.46)	1.80 (0.70)	64.55 (0.87) E	68.85 (2.04) D	795.36 (4.18) CD
63.78 (0.37)	2.39 (0.10)	66.16 (0.86) F	64.97 (2.40) C	784.32 (18.23) BC
62.82 (1.43)	1.77 (0.50)	64.69 (0.93) E	61.54 (2.52) B	758.02 (16.49) AB
69.88 (0.62)	1.96 (0.35)	71.84 (0.79) H	58.67 (1.61) AB	736.06 (24.91) A
68.69 (0.37)	1.59 (0.58)	70.28 (0.81) G	56.54 (0.49) A	731.70 (42.40) A
59.66 (0.29)	1.77 (0.10)	61.44 (0.36) C	69.74 (2.34) D	813.29 (25.58) CDE

*The numbers in phrantheses are standard deviations
**The same letters on the same columns show that statistically there is not a significant difference within a 95% confidence interval.

The general physical and strength properties of both Calabrian and Monterey pine pulps are given in Table 10. It can be seen that both pulps have marginally similar bulk properties and are in the chemical pulp range. However, the Monterey pulp has approx. 2.5 degree higher brightness properties compared to Calabrian pine. Moreover, it can be clearly realized that Calabrian pine pulps have usually higher strength properties than Monterey pine pulps at similar pulping conditions. Here, Calabrian pine is considered to have longer fiber length than Monterey pine (Tank et al., 1990).

Table 10. The general physical and strength properties of pulps.

Wood species	Bulk (cm^3/g)	Brightness (%)	Tensile index (N.m/g)	TEA (J/m^2)	Tear index ($mN.m^2/g$)	Burst index ($kPa.m^2/g$)
Calabrian pine	1.19 (0.02)	16.55 (0.19)	75.44 (3.77)	90.34 (6.50)	5.6 (0.11)	3.59 (0.24)
Monterey pine	1.34 (0.03)	19.09 (0.39)	66.92 (2.35)	85.84 (4.28)	5.4 (0.18)	3.25 (0.12)

Figures 1 and 2 shows sulfidity and $NaBH_4$ addition effects on total pulp yield of both Calabrian and Monterey pine, respectively. As seen in both Figures, the marked effects on not only $NaBH_4$ addition but also sulfidity for both species are shown (Fig.1).

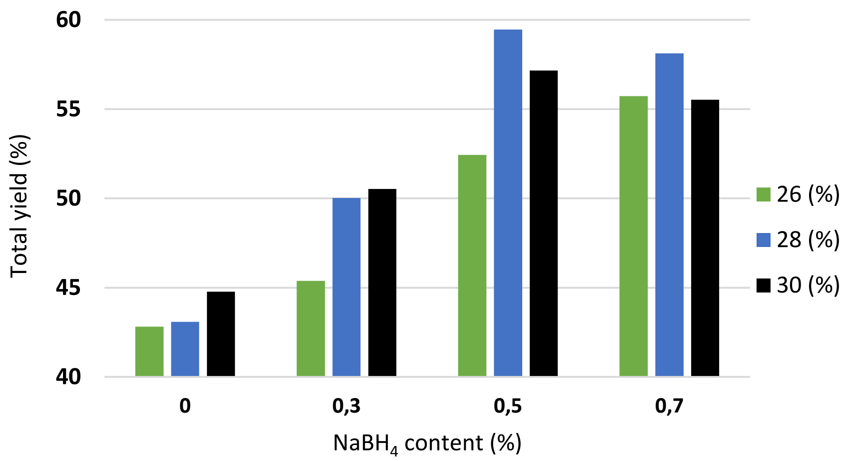

Figure 1. The sulfidity and $NaBH_4$ addition effects on yield for Calabrian pine.

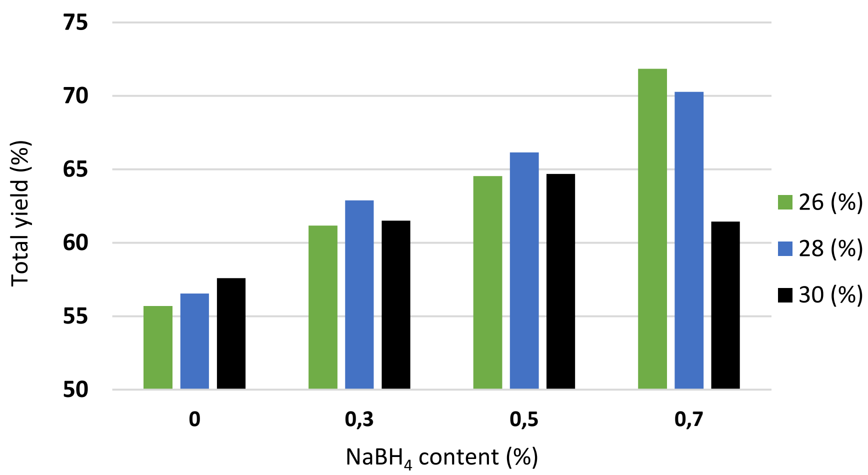

Figure 2. The sulfidity and $NaBH_4$ addition effects on yield for Monterey pine.

Figures 3 and 4 shows effects of $NaBH_4$ addition into Kraft pulping process on delignification (kappa number) for Calabrian pine (Fig.3) and Monterey pine (Fig.4), respectively. For Calabrian pine; it was realized that the lowest kappa number of 42.05 was found at 28% sulfidity and 0.5% $NaBH_4$ level whereas the highest kappa number of 65.78 was found at 30% sulfidity without $NaBH_4$ addition. For Monterey pine; it was realized that the lowest kappa number of 56.54 was found at 28% sulfidity and 0.7% $NaBH_4$ level whereas the highest kappa number (78.24) was found at 30% sulfidity without $NaBH_4$ addition. With having these results it is reasonable to suggest that $NaBH_4$ addition to Kraft cooking has improving effects on yield (Fig. 1 and 2) and delignification (Fig. 3 and 4) for both pine species.

The decrease in the kappa numbers of Kraft pulps can be explained with the fact that $NaBH_4$ accelerates delignification by keeping carbohydrates during the pulping process. Due to the effect of $NaBH_4$ on the decrease of kappa number, it's considered that expected kappa number can be reached sooner and energy saving is possible.

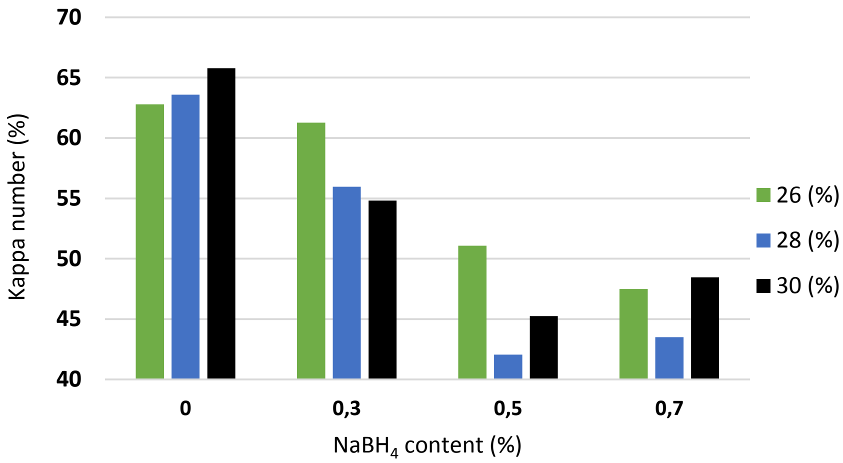

Figure 3. The effects of sulfidity and $NaBH_4$ addition on kappa number for Calabrian pine.

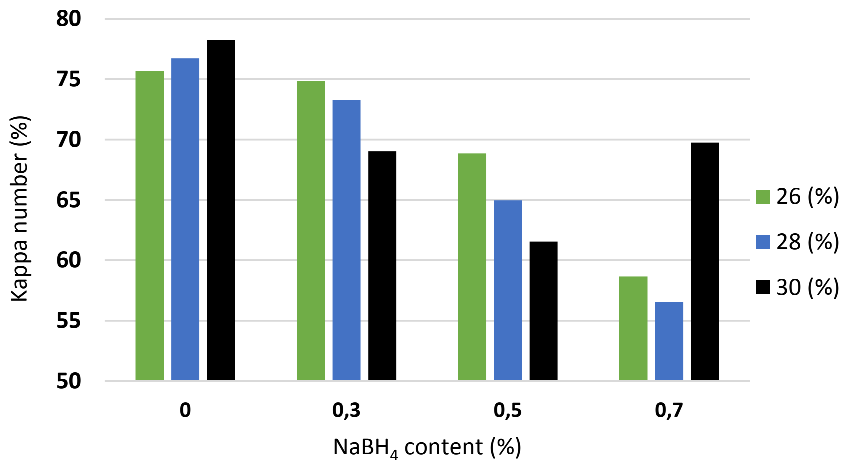

Figure 4. The effects of sulfidity and $NaBH_4$ addition on kappa number for Monterey pine.

It is well known that a certain number of ether bonds (α-O-4 and β-O-4) within the lignin macromolecule must be cleaved to dissolve lignin during pulping (delignification). However, in all reaction conditions, Calabrian pine pulps have 2-20 lower kappa numbers (residual lignin) compared to the Monterey pine. It is reasonable to suggest that $NaBH_4$ effects on lignin for Calabrian pine are better than the ones for Monterey pine.

However, it was assumed that the combination of boron ($NaBH_4$) compound with alkali condition acted on lignin is as follows: The $NaBH_4$ probably promoted the penetration of the alkali into the cell wall following the breakdown of lignin. However as mentioned above, Hafızoğlu and Deniz (2007) proposed that $NaBH_4$ is a reducing agent that is able to block reducing end-groups of carbohydrates (i.e. hemicelluloses) so it converts the aldehyde and keto group to the hydroxyl group by reducing easily.

Figures 5 and 6 shows the effect of $NaBH_4$ addition to Kraft pulping process on viscosity for Calabrian pine (Fig. 5) and Monterey pine (Fig. 6), respectively. It was realized that the highest viscosity value 948.02 cm^3/g was found at 26% sulfidity without $NaBH_4$ whereas the lowest viscosity 771.19 cm^3/g was found at 28% sulfidity and 0.5% $NaBH_4$ addition for Calabrian pine. However, the highest viscosity value of 880.89 cm^3/g was found at 26% sulfidity without $NaBH_4$ for Monterey pine.

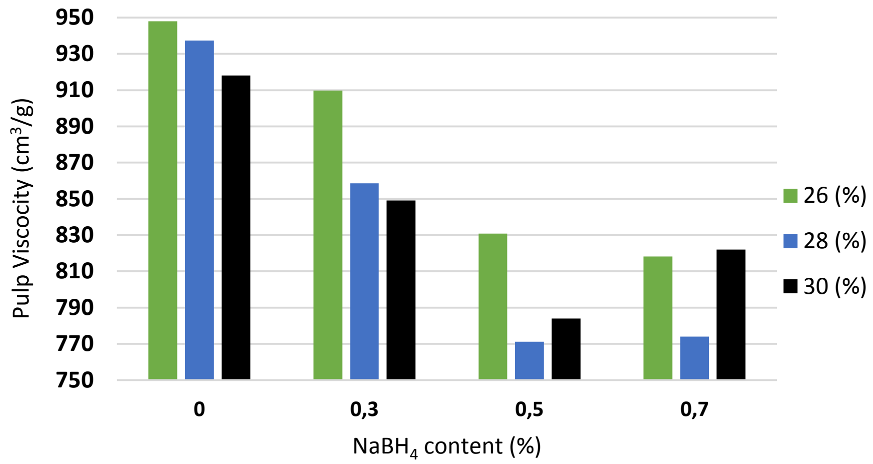

Figure 5. The sulfidity and $NaBH_4$ addition effects on viscosity properties for Calabrian pine.

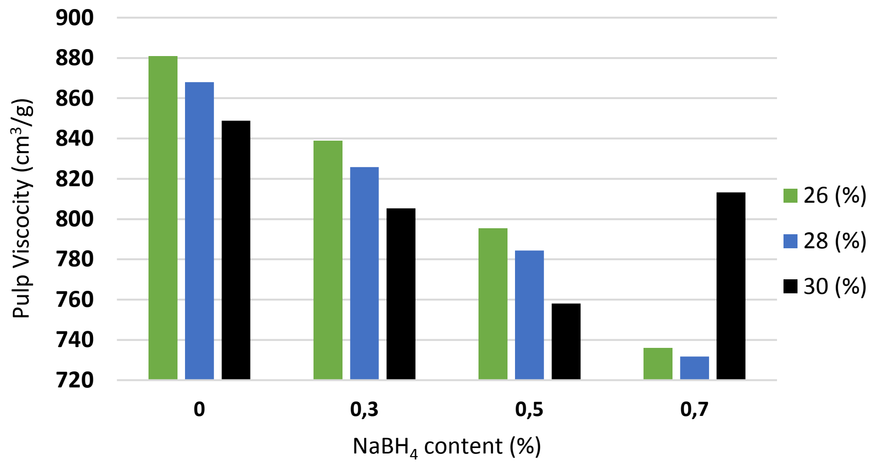

Figure 6. The sulfidity and $NaBH_4$ addition effects on viscosity properties for Monterey pine.

4. Summary

The experimental results indicated that improving delignification and increasing yield could be obtained from both Calabrian and Monterey pine with $NaBH_4$-kraft pulping conditions. The addition of $NaBH_4$ to Kraft cooking liquors was found to offer advantages. This approach produced a substantially greater degree of pulp yield than conventional Kraft pulping under the same conditions. The best $NaBH_4$-kraft pulping condition for the Calabrian pine was found with 16% AA, 28% sulfidity and 0.5% $NaBH_4$ addition whereas the best conditions for Monterey pine was found with 20% AA, 26% sulfidity and 0.7% $NaBH_4$ level. The laboratory-scale studies reported that this may be applied to improve industrial-scale processes.

Acknowledgement

This work was carried out while A. Saraçbaşı was working in Central Anatolia Forestry Research Institute. The authors wish to thank the financial support received for this research from Ministry of Forestry and Water Affairs, General Directorate of Forestry, Central Anatolia Forestry Research Institute, Ankara, Turkey, Project number: 23.7131/2010-2012-2014.

Literature

Biermann, CJ. 1993. Essentials of Pulping and Papermaking, *Academic Press Inc*. San Diego, CA. pp.653.

Bujanovic, B., Cameron, J.H., Yilgor, N. 2003. Comparative studies of Kraft and Kraft-borate pulping of black spruce, *Journal of Pulp and Paper Science*, 29 (6): 190-196.

Bujanovic, B., Cameron, J.H., Yilgor, N. 2004. Some properties of Kraft and Kraft-borate pulps of different wood species, *Tappi Journal*, 3 (6): 3-6.

Çöpür, Y., Tozluoğlu, A. 2007. A comparison of kraft, PS, kraft-AQ and kraft-$NaBH_4$ pulps of brutia pine. *Bioresource Technology*, 99 (5): 909–913.

Göksel, E. 1981. Kızılçamın lif morfolojisi ve odunundan sülfat selülozu elde etme olanakları üzerine araştırmalar, İ.Ü. Orman Fakültesi Dergi Serisi, Seri: A, 31 (1): 203-216, (Turkish), Istanbul-Turkey.

Gülsoy S.K., Eroğlu H. 2011. Influence of sodium borohydride on Kraft pulping of European black pine as a digester additive. Industrial & Engineering Chemistry Research50 [4]: 2441–2444

Hafızoğlu, H., Deniz, İ. 2007. Odun kimyası, K.T.Ü. Orman Fakültesi Yayınları, Trabzon.

İstek A., Gönteki, E. 2009. Utilization of sodium borohydride ($NaBH_4$) in kraft pulping process, *Journal of Environmental Biology*, 30(6): 5-6.

Khaustova, L. G., Ioffe, G. M., Pen, R. Z., Ignat'eva, N. I. 1971: Pulp from larchwood: kraft cooks of larchwood with liquors containing reducing agents and sulfur. Izv. VUZ, Lesnoi Zh. 14, no. 3: 101–1066 p.p.

Nelson, P.J., Irvine, G.M. 1992. Tearing resistance in soda-AQ and kraft pulps, Tappi Journal, 75(1)

Özdemir, F., Tutuş, A. 2013. Effects of fire reterdants on the combustion behavior of high-density fiberboard, BioResources 8 (2):1665-1674.

Pettersson, S.E., Rydholm, S.A. 1961. Hemicelluloses and paper properties of birch pulps, Part 3. Svensk Papperstidning, 64 (1), 4-17.

Scan Tests, 1973. Scandinavian Pulp Paper and Board Testing Committees, Stockholm.

Smook, GA. 1994. Handbook for pulp & paper technologists, *Angus Wilde Publications.* Canada.

Tank T., Göksel E., Cengiz M., Gürboy K., 1990 Hızlı gelişen bazı iğne yapraklı ağaç türlerinin lif ve kağıt teknolojisi yönünden incelenmesi, İstanbul Üniversitesi Orman Fakültesi Dergisi, 40, 40-54.

Tappi Standards, 1972. Standard methods related in pulp and paper Technical Ass. Pulp and Paper Ind. Atlanta, Georgia, U.S.A.

Tutuş, A. and Usta, M. 2004. Bleaching of chemithermomechanical pulp (CTMP) using environmentally friendly chemicals. J. Environ. Biol., 25,141-145.

Tutuş, A., Çiçekler, M., Deniz, İ. 2012. Using of burnt red pine wood for pulp and paper production, (Turkish, Abstract in English), KSU Journal of .Engineering Sci., Special Issue, 90-95.

Tutuş, A., Çiçekler, M., Ayaz, A., 2016. Evaluation of apricot (*Prunus armeniaca* L.) wood on pulp and paper production, (Turkish, Abstract in English), Turkish Journal of Forestry, 17(1): 61-67. DOI: 10.18182/tjf.29700.

Virkola N.E., Pusa R., Kettunen J. 1981. Neutral sulfite AQ pulping as an alternative to kraft pulping. In: Goyal G.C. (ed.), Anthraquinone Pulping: A TAPPI press Anthology of Published Papers. Atlanta-1997: 401–405.

Young, RA. 1997. Pulp and paper, In: Paper and composites from agro-based resources, R. M. Rowell, R. A. Young and J. K. Rowell (Eds) *CRC Press Inc,* Boca Raton, Florida, pp.137-236.